

Influence of Cu^{2+} and Cu^{3+} Cations on the Optical Properties of $\text{Bi}_{12}\text{SiO}_{20}:\text{Cu}$

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The absorption spectrum of $\text{Bi}_{12}\text{SiO}_{20}:\text{Cu}$ is measured in the spectral region 0.195–2.95 eV. The validity of the Urbach rule (2.08–2.95 eV) has been also verified. The photochromic effect of these samples in far IR region is investigated. The energy level diagram of Cu^{3+} cations in Bi-octahedrons is presented.

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1. Introduction

The copper cations influence positively on the properties of doped sillenites $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) and their practical applications [1]. This impurity increases photorefractive and photochromic effects in these single crystals. Cu cations optimize the parameters of devices of optical recording of information [2–6] and they are used to record holograms in IR region.

The structure of Cu local states is complicated in the forbidden band of BSO:Cu. Its investigation and the determination of electronic transitions in the formation of the absorption spectrum are of great scientific interest. The reason is in the processes of redistribution of charge carriers between the local impurity levels. This fact is important for clarifying the mechanisms of the optical information processing.

2. Experimental details

BSO single crystals, non-doped and doped with Cu, were grown from stoichiometric melts $\text{Bi}_2\text{O}_3:\text{SiO}_2 = 6:1$ using the Czochralski method under conditions described in detail elsewhere [7, 8]. High purity of Bi_2O_3 , SiO_2 , and Cu_2O_3 oxides were used for synthesis and doping. BSO:Cu was prepared with Cu content of 0.02 mol.% in the starting melt.

The optical absorption spectra were measured on double-side polished parallel crystal plates using a SPM-2 monochromator within accuracy of ± 2 nm. Prior to the measurement, all investigated samples were re-excited either optically by UV light illumination (Hg lamp) or thermally by annealing at 500°C in air for 20 min for photochromic effect studies. The UV exposure state will be denoted herein after as the illuminated state and the

temperature annealed state both will be called the annealed state. The measurements in the far IR region are realized by Shimadzu Fourier transform infrared spectrophotometer IRAffinity-1.

3. Results and discussion

The Urbach formula is expressed by the equation $\ln \alpha = A + B(\hbar\omega/T)$, where α is the absorption coefficient, A and B are constants, T is the temperature. The constant B is connected with the parameter $\sigma(T)$ by the dependence $B = \sigma(T)/k$, where k is the Boltzmann constant. $\sigma(T)$ characterizes the slope of the absorption edge. The value of $\sigma(T)$ is 0.28 for $\text{Bi}_{12}\text{SiO}_{20}$ and $\sigma(T)$ is 0.1 in the case of $\text{Bi}_{12}\text{SiO}_{20}:\text{Cu}$. On the other hand, the magnitude $W_d = kT/\sigma$ [9] describes the broadening of the absorption edge due to the dynamic disorder. When the temperature is higher, the absorption edge has a larger width due to the dynamic disorder in the crystal lattice. $W_d = 92$ meV for undoped BSO and $W_d = 259$ meV for BSO:Cu. Therefore we can resume that the absorption edge of the doped sample has bigger dynamic disorder in the crystal lattice because of Cu presence.

The approximation of experimental data shows $\sigma(T) = \sigma_0(2kT/h\nu_0) \tanh(h\nu_0/2kT)$, where $h\nu_0$ is the energy of effective phonons strongly interacting with photons and σ_0 is the high temperature constant [10]. The magnitude $h\nu_0$ for our investigated crystals corresponds to the energy $h\nu_0 = 31.7$ meV of longitudinal optical phonons ($\omega = 257$ cm^{-1}) which are observed in IR absorption spectra of BSO [11]. In our situation, the obtained values of σ_0 are as follows: $\sigma_0 = 0.28$ ($\text{Bi}_{12}\text{SiO}_{20}$) and $\sigma_0 = 0.1$ ($\text{Bi}_{12}\text{SiO}_{20}:\text{Cu}$).

When we compare the values of σ_0 for our samples with the values of the same constant, obtained in [12], we can summarize that our undoped sillenite has a surplus of Bi ions in the crystal lattice. The dependence $g = 2/3\sigma_0$ determines the strength of the electron-phonon interaction [10]. When g is bigger than 1 the electron-phonon

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interaction is strongly. This strength has a value $g = 2.38$ for undoped BSO and $g = 6.67$ for BSO:Cu. Therefore we can note that Cu cations increase this interaction in the crystal lattice.

The magnitudes $\sigma(T)$, σ_0 , W_d and g are calculated by the linear dependence in Fig. 1. The Cu cations play role of acceptors in doped BSO because of their small concentration. In this way, Cu cations compensate the deep donor centers — the own defects of crystal lattice $\text{Bi}_{\text{Si}}^{5+}$ occupying the Si^{4+} positions. The absorption of the type: impurity \leftrightarrow band decreases and we observe the lightening of the crystal plate. This absorption realizes between the impurity level in the forbidden band and the conduction band or the valence band in the region of the absorption edge.

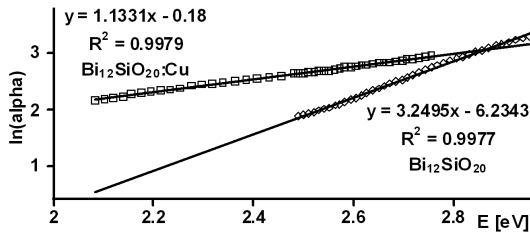


Fig. 1. Urbach's rule of undoped $\text{Bi}_{12}\text{SiO}_{20}$ and Cu doped $\text{Bi}_{12}\text{SiO}_{20}$.

Figure 2a–c shows the absorption spectra of Cu-doped $\text{Bi}_{12}\text{GeO}_{20}$ (BGO) crystals and the first and second derivate calculations of the absorption coefficient $\alpha(E)$. The calculation of the first derivative determines the number of electron transitions in Cu^{3+} cation and the second derivative calculation determines the exact energy position of the copper levels. The energy diagram is presented in Fig. 3 and will be discussed further.

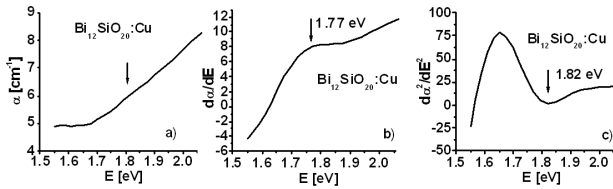


Fig. 2. The absorption spectrum of BSO:Cu in the spectral region 1.5–2.1 eV (a); first derivative of $\alpha(E)$ for BSO:Cu (b); second derivative of $\alpha(E)$ for BSO:Cu (c).

The EPR data of Cu doped BGO (BGO:Cu) show that Cu^{2+} cations are situated in T_d positions of the elementary cell [13]. Chevrier et al. present EPR investigation of BGO:Cu [13] and these data prove predominantly the localization of Cu^{2+} cations in Bi-positions of these crystals. It can be assumed that Cu^{3+} cations substitute Bi^{3+} in the oxygen pseudo-octahedrons [14]. The ionic radius of Bi^{3+} is bigger than this of $\text{Cu}_{\text{Bi}}^{2+}$ ($3d^9$) and $\text{Cu}_{\text{Bi}}^{3+}$ ($3d^8$). This is the reason of the deformation of the oxygen octahedrons. In our case, the octahedron is extended along

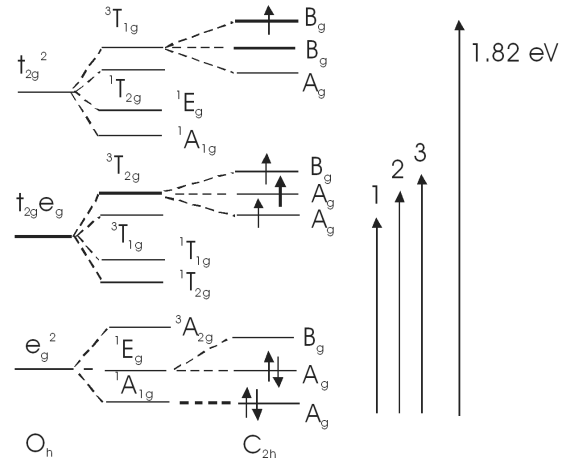


Fig. 3. Energy level diagram of $3d$ electrons in Cu^{3+} cation.

the z -axis. The Jahn–Teller effect and spin–orbit interaction eliminate the degeneration in the complex $[\text{CuO}_6]^{3+}$. The dynamical Jahn–Teller effect causes a tetragonal deformation (D_{4h}) [15] of the complex $[\text{CuO}_6]^{3+}$ at the room temperature. Two ligands are mixed away from Cu^{3+} cation in D_{4h} . This is due to the difference of the crystal field strength between the ligands X and Y in MX_4Y_2 . The symmetry C_{2h} is a consequence of the spin–orbit interaction. The transition $^1A_{1g} \rightarrow ^3T_{1g}$ at 1.82 eV (Fig. 3) is due to the electron transition in Cu^{3+} ions [14]. This unpaired electron is on the degenerate energy state x^2-y^2 because of the elongation of the octahedron [16]. The orbital $d_{x^2-y^2}$ is σ -orbital of the ligands which are connected with Cu^{3+} cation.

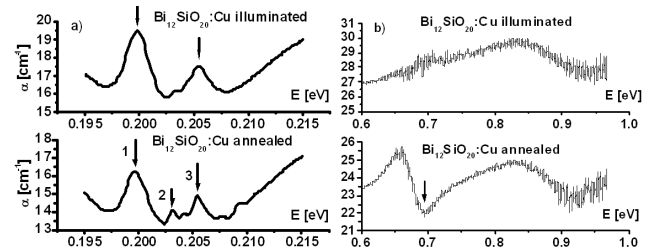


Fig. 4. The absorption spectra of $\text{Bi}_{12}\text{SiO}_{20}:\text{Cu}$ in the illuminated and the annealed state: (a) in the spectral region 0.195–0.215 eV; (b) in the spectral region 0.6–1 eV.

It is well known that transition metal compounds (TMC) have two main groups of electrons determining their properties. These are the electrons of partially filled d -shells of the transition metal (TM) and the p -electrons of the oxygen. TM ions as Cu cations prefer to retain a lower valence (the higher occupation of d -shell) at the expense of creating holes on oxygen. The photochemical reactions are responsible for the change of the charge of the impurity cations in the transition in the metastable photoinduced state. This change is realized by the scheme

$\text{Cu}_{\text{Bi}}^{2+}-e \rightarrow \text{Cu}_{\text{Bi}}^{3+}$. The neutrality of the charge is realized by O^- centers-holes [13].

In this way the paired centers $\text{Cu}_{\text{Bi}}^{2+}-\text{O}^-$ are responsible for the photochromic effect in our doped crystals (Fig. 4). The theoretical calculations show that the optical transitions in Cu^{3+} cations give three absorption bands around 0.31–0.37 eV [17]. Our absorption spectra in the far IR region confirm the existence of these three bands which are shifted in the spectral region 0.195–0.215 eV. The transitions 1, 2, and 3 (Fig. 4a) correspond to the three electron transitions 1, 2, and 3 in Cu^{3+} cations in Fig. 3. These three absorption bands manifest when the crystal is in an annealed state and they are two when the crystal is illuminated. The electron transition ${}^2E_g \rightarrow {}^3T_{1g}$ [14] at 0.8 eV is realized because of Cu^{2+} cations in Bi positions (Fig. 4b). $\text{Bi}_{12}\text{SiO}_{20}$ single crystals are impoverished of Bi ions when the samples are annealed in oxygen environment. After that these ions are deposited on the crystal surface and Bi is vaporized from the surface. This fact provokes the change at 0.7 eV in the annealed state of BSO:Cu (Fig. 4b).

4. Conclusions

The Cu^{2+} cations show their influence in the Urbach rule region and the influence of Cu^{3+} cations is in the visible spectral region. The Cu^{2+} cations decrease the number of $\text{Bi}_{\text{Si}}^{3+}$ defects in the region of the absorption edge and we observe lightening of the crystal. The results of our experiment are as follows: (1) The Cu^{3+} cations give three absorption bands in the spectral region 0.195–0.215 eV when BSO:Cu is in the annealed state; (2) there is a reduction of Bi ions in the crystal lattice after annealing in the oxygen environment at 0.7 eV.

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